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Conductivity of Polyacrylonitrile Based Lithium Polymer Electrolytes

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13. ABSTRACT (Maximum 200 words) Preparation of solid state polymer lithium electrolytes based on polyacrylonitrile (PAN) have achieved room temperature conductivities equal to that of liquid organic electrolytes. Polymer films of ethylene carbonate, propylene carbonate, PAN, and lithium salts have yielded conductivities as high as 0.004 S/cm at 25 deg C. These high conductivities make the use of polymer electrolytes a viable possibility in advanced batteries. Reported here are film preparation technique, conductivities from -70 to 70 deg C, and Vogel-Tammann-Fulcher (VTF) relationships.				
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INTRODUCTION

The use of solid polymer electrolytes (SPE) in rechargeable lithium batteries is currently being widely investigated. Polymer electrolytes can be prepared into very thin films possessing large surface area yielding high power densities. An energy advantage of a solid flexible electrolyte is its ability to enable the design of more volume efficient battery configurations. In an electrochemical cell, especially in a reversible cell, a flexible electrolyte can accommodate the volume changes that occur with charge/discharge cycles. Polymer electrolytes can increase cell safety by preventing ignition by acting as a shut down separator, if thermal runaway should occur within a cell. A thin Li^+ ion conducting polymer film acts as both the electrolyte and a separator between the lithium anode and a lithium insertion compound as the cathode. The use of high energy cathode films of reversible compounds such as LiCoO_2 , LiNiO_2 , LiMn_2O_4 , V_2O_5 , or V_6O_{13} with thin lithium foil anodes and the structural flexibility of polymer electrolytes make the lithium polymer battery a promising candidate for advanced battery systems for electric vehicles (EV) or consumer/military electronics applications.

One of the first polymer electrolyte chemistries consisted of poly(ethylene oxide) PEO-LiX complexes (1,2) which need to operate at around 100°C . New multiphase systems involve adding plasticizing solvents to PEO-LiX or trapping liquid electrolyte solutions in a polymer matrix to form a "gel" electrolyte. The latter more "liquid like" chemistries can operate at room temperature and therefore are of interest for further research. One of the basic fundamental problems in the development of solid state ionic materials based on polymers is the conductivities of these materials. Recently, room temperature conductivities as high as $10^{-3} \text{ S cm}^{-1}$ have been reported for polyacrylonitrile (PAN) based lithium salt complexes (3). It is ionic conductivity measurements on this chemistry that is the focus of this report.

EXPERIMENTAL

The preparation of the solid gel electrolytes involved the immobilization of LiClO_4 , LiAsF_6 , or $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in ethylene carbonate (EC) and propylene carbonate (PC) mixtures with PAN. The LiAsF_6 (Lithco "Lectro-salt") and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (3M) were dried under vacuum at 60°C for 24 h.; LiClO_4 (Alfa reagent grade) was recrystallized in distilled water, then dried under vacuum at 150°C for 24 h. PC (Burdicke and Jackson) was dried with type 4A molecular

sieves for 48 h then distilled under vacuum. EC (Fluka AG) was fractionated under vacuum. Dimethyl carbonate (DMC) (Burdick and Jackson) was fractionated in an argon atmosphere. Karl Fisher titration for EC, PC, and DMC indicated water contents of <24 ppm. Poly(acrylonitrile) (Polyscience Inc.) with an average molecular weight of 150,000 was dried under vacuum at 60°C for 48 h.

The liquid electrolyte EC:PC:LiX was prepared in a vial with a stirring bar. PAN powder was then added and the mixture stirred to ensure wetting of the PAN. The mixture was heated slowly in an oil bath to 100°C, avoiding overheating and decomposing the PAN. The mixture turned to a clear highly viscous gel and was cast between glass plates, with 0.25 mm spacers, and allowed to cool. The resulting polymer electrolyte was an elastomeric mechanically stable film. Two general film compositions were prepared with mole percentages of 40EC:34.75PC:21PAN:4.25LiX (17.6:1 EC+PC:LiX) and 38EC:33PC:21PAN:8LiX (8.8:1 EC+PC:LiX). Variations to these compositions include the use of DMC with EC/PC mixtures, the addition of ground molecular sieves to form a composite film, and a film with a lower concentration of PAN (12%).

Electrolyte conductivities were determined from ac impedance measurements using an EG&G PAR model 388 impedance system with a frequency range of 5 Hz to 1000 kHz. The test cell was made of ceramic with an electrode configuration of SS/SPE/SS. A thermocouple was in close proximity to the SPE in the cell. The cell assembly was inserted into a wide-mouthed glass reaction vessel packed with molecular sieves, and nitrogen bubbled through. The temperature testing (70°C to -70°C) was performed in a Tenney environmental chamber. All chemical storage, film casting, and cell assembly was performed in a Vacuum Atmospheres argon-filled dry box.

RESULTS AND DISCUSSION

For polymer electrolytes to be of practical use, Li-ion mobility must be high enough to enable useful rate capabilities in lithium batteries. As a general comparison of two types of polymer electrolyte chemistries, Figure 1 shows an Arrhenius plot of the ionic conductivities of PEO-LiClO₄ film, a PAN:EC:PC:LiClO₄ film, and a EC:PC:LiClO₄ liquid electrolyte. The PAN-based electrolyte film demonstrates conductivities approaching that of the liquid and a significant increase in ion mobility over the PEO electrolyte. It is this result, first demonstrated by Abraham and Alamgir for this chemistry (3), that makes a mechanically stable free-standing film a possible battery

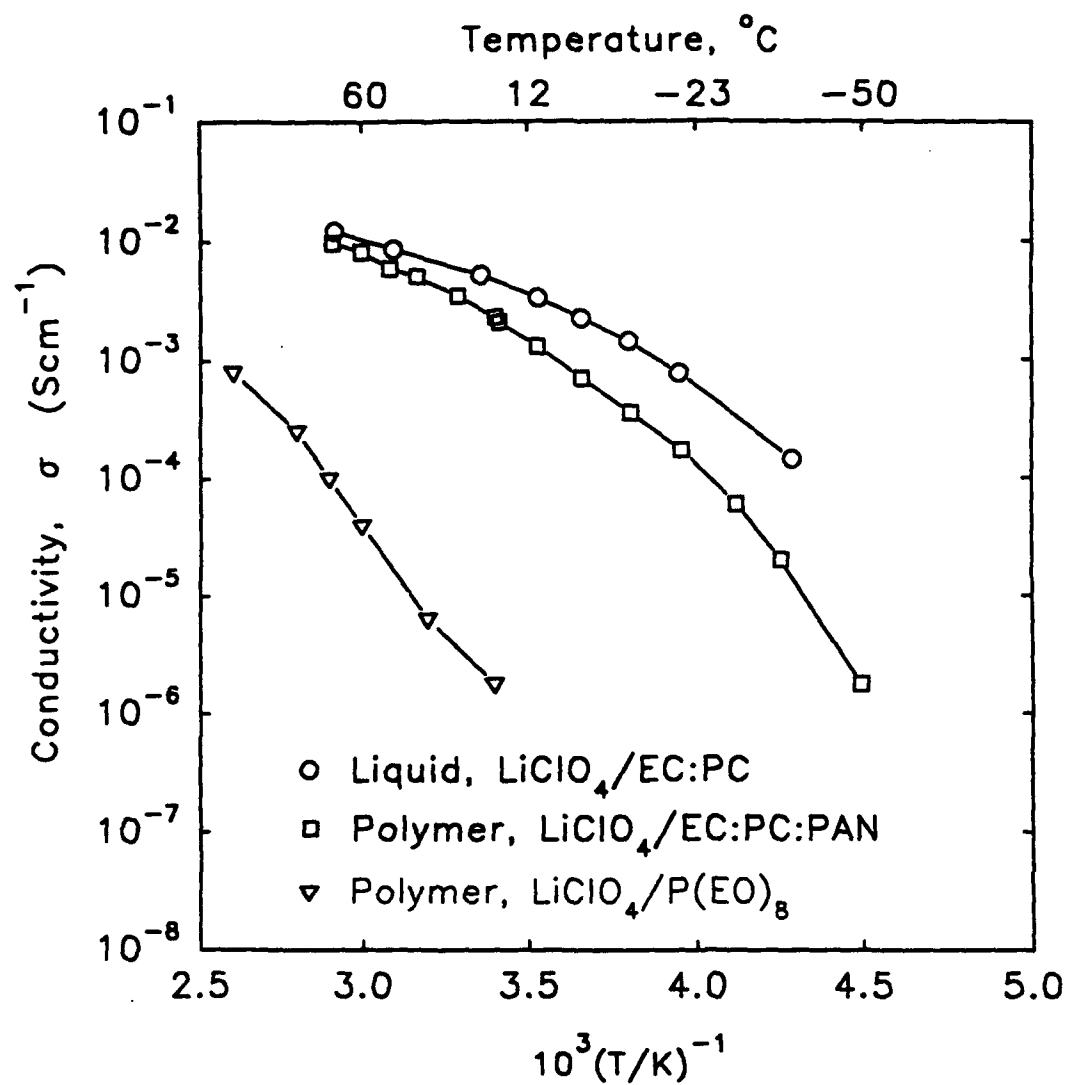


Figure 1. Arrhenius plot of electrolyte conductivities.

electrolyte. The difference in conductivity of the PAN-based electrolyte and the liquid at decreasing temperatures is due to the lower viscosity of the polymer.

Having established that PAN-based films can be prepared and can produce ionic conductivities close to liquid organic electrolytes, further studies of Li-ion mobility in these types of electrolytes were performed. Table 1 lists the polymer electrolyte molar compositions, solvent:LiX ratio, and conductivities at 25°C of the films studied.

TABLE 1. Electrolyte Conductivities at 25°C

ELECTROLYTE	Solvent:LiX	CONDUCTIVITY (S cm ⁻¹)
45EC:45PC:LiClO ₄ (liquid)	9:1	5.2 x 10 ⁻³
38EC:33PC:21PAN:8LiClO ₄	8.8:1	2.9 x 10 ⁻³
40EC:34.75PC:21PAN:4.25LiClO ₄	17.6:1	4.5 x 10 ⁻⁴
56.5:EC:23PC:16PAN:4.25LiN(CF ₃ SO ₂) ₂	17.6:1	2.0 x 10 ⁻³
40EC:34.75PC:21PAN:4.25LiAsF ₆	17.6:1	3.7 x 10 ⁻³
40EC:34.75PC:21PAN:4.25LiAsF ₆ :5wt%3Å	17.6:1	1.6 x 10 ⁻³
33EC:28PC:13.5DMC:20PAN:5.5LiAsF ₆	13.5:1	9.9 x 10 ⁻⁴
44.3EC:39PC:12PAN:p4.7LiAsF ₆	17.6:1	2.8 x 10 ⁻³
38EC:33PC:21PAN:8LiAsF ₆	8.8:1	1.0 x 10 ⁻³

In Figure 2, the conductivities of three LiX salt complexes, LiAsF₆, LiClO₄, and LiN(CF₃SO₂)₂ with EC:PC:PAN, are shown. As in liquid organic electrolytes, the LiAsF₆ electrolyte gives the highest conductivity. The imide, LiN(CF₃SO₂)₂, known as a high temperature stabilizing salt, demonstrated poor conductivity at low temperatures. This is believed to be due to precipitation of the imide salt from the EC:PC mixture resulting in loss of lithium ions for charge transfer.

The arrhenius plots in Figure 3 show the conductivities of three chemical variations with the LiAsF₆ electrolyte. Changing the solvent to LiAsF₆ ratio from 17.6:1 to 8.8:1 (i.e., doubling the amount of salt while holding the PAN concentration at 21 mole percent) lowers the conductivity over the whole temperature range. This again is a viscosity effect on the ionic mobility. The addition of DMC, which in liquids makes the electrolyte more stable with the lithium metal anode, lowers the conductivity. This is expected since LiAsF₆/DMC electrolyte has a lower conductivity than

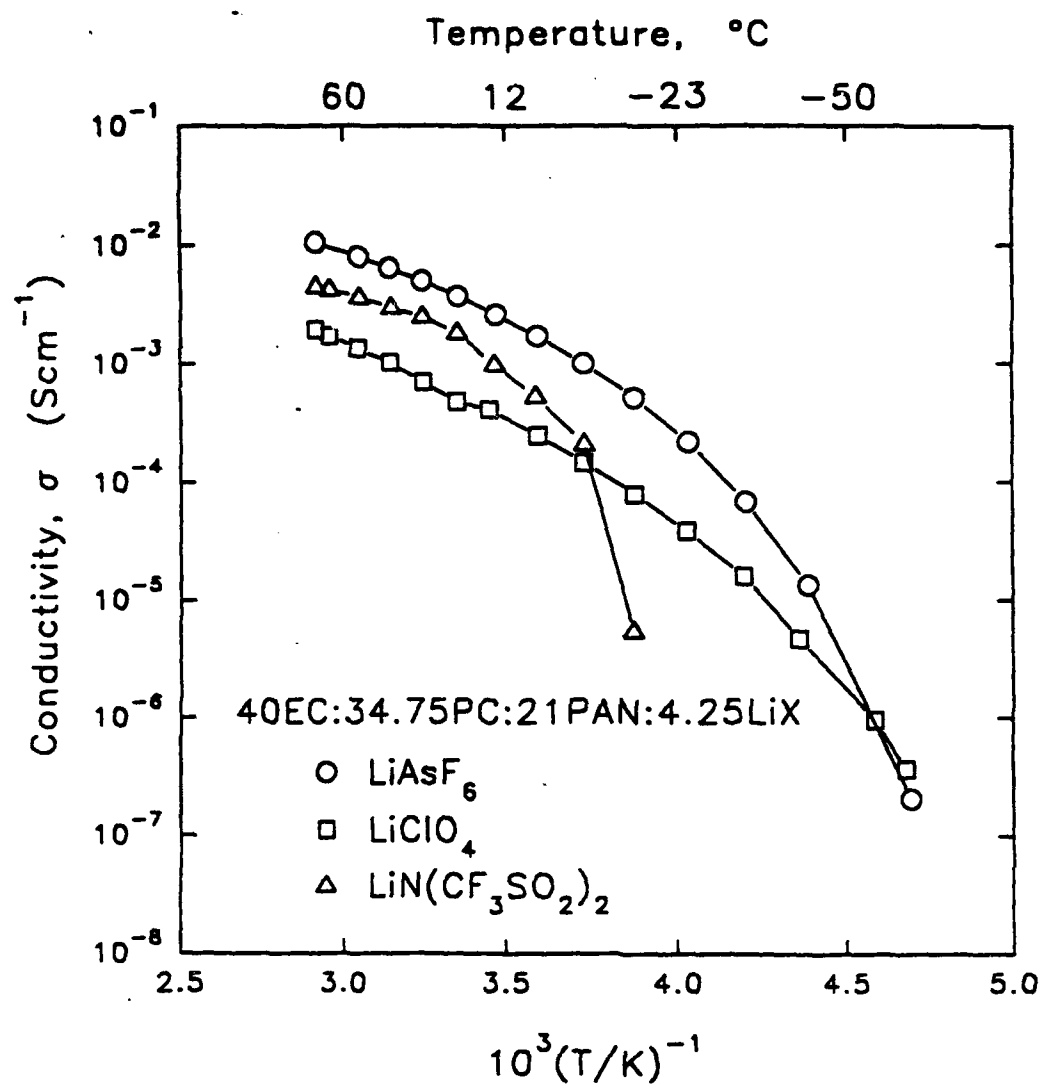
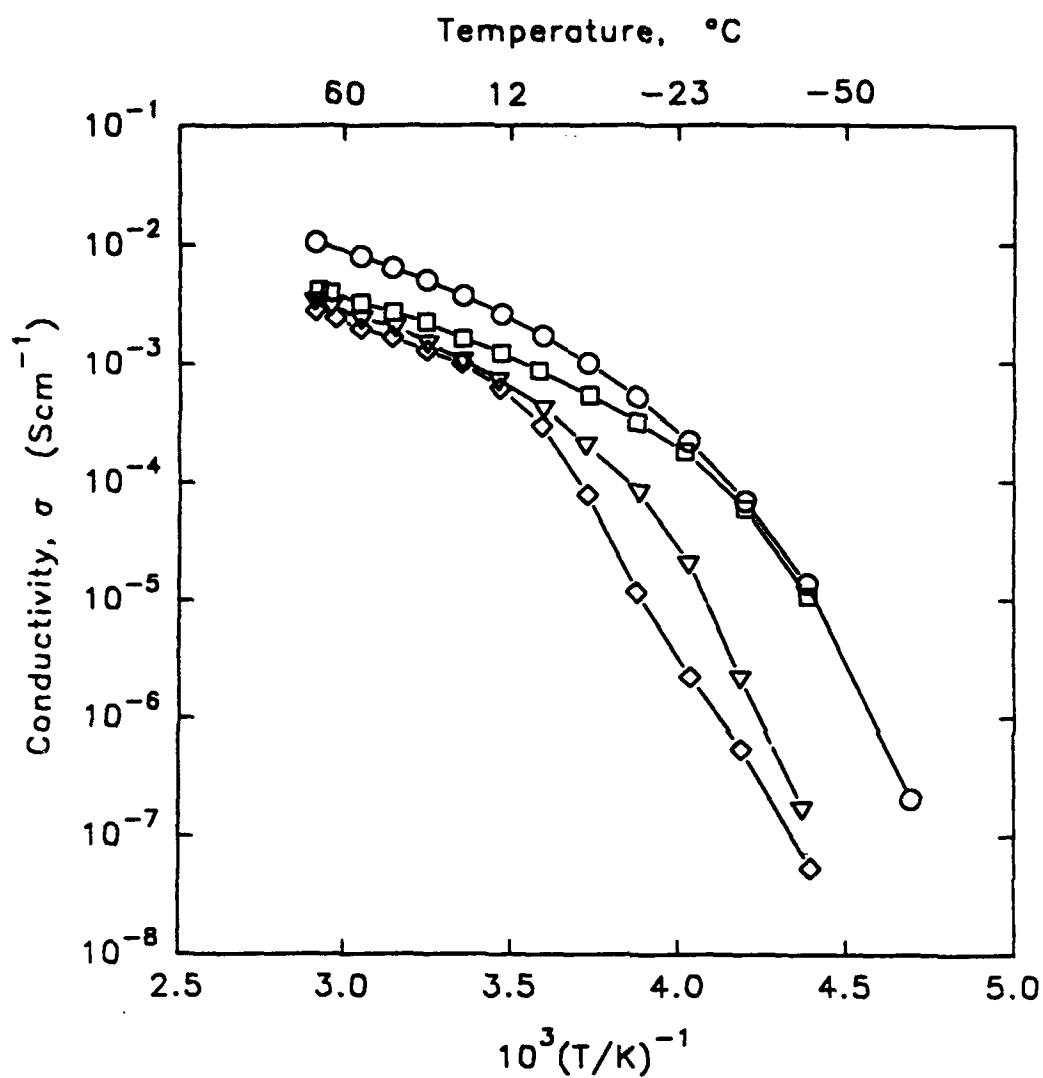


Figure 2. Arrhenius plot of electrolyte conductivities.



- EC:PC:PAN:LiAsF₆ (17.6:1)
- EC:PC:PAN:LiAsF₆ (17.6:1) w/5wt% 3A sieves
- ▽ EC:PC:PAN:LiAsF₆ (8.8:1)
- ◇ EC:PC:DMC:PAN:LiAsF₆ (17.6:1)

Figure 3. Arrhenius plot of electrolyte conductivities.

LiAsF₆/EC:PC in liquids due to its much lower dielectric constant (ϵ : EC=39.6, PC=64.9, DMC=3.1). A film with a 12% concentration of PAN was prepared. Its conductivity (seen in Figure 4) at lower temperatures was greater than films prepared with 21% PAN. This is expected since the film with less PAN is more liquid like. The electrolyte was "wetter," but still had the physical integrity of a solid film.

All the arrhenius plots for the gel electrolytes exhibit significant curvature, which is characteristic of Vogel-Tammann-Fulcher (VTF) behavior (1). The VTF relationship is an application of free-volume distribution to conductivity in polymer dynamics and is expressed by the equation

$$\sigma = AT^{-1/2}\exp[-E_a/(T-T_0)] \quad (1)$$

where A is a prefactor related to the transport coefficient, T_0 is the idealized temperature corresponding to zero configurational entropy, and E_a is the activation energy for charge transport within the gel electrolytes. Table 2 gives these calculated values for some of the electrolytes studied.

TABLE 2. VTF Equation Values

ELECTROLYTE	A	T_0 (°C)	E_a (eV)
EC:PC:LiClO ₄ (Liquid)	2.68	176	0.036
EC:PC: PAN:LiClO ₄ (17.6:1)	5.38	130	0.093
EC:PC: PAN:LiAsF ₆ (17.6:1)	4.12	176	0.043
EC:PC: PAN:LiAsF ₆ (8.8:1)	5.10	162	0.066

Figure 5 shows the straight line VTF plots from which the activation energies were determined. These calculations were performed over a temperature range of -20°C to 70°C. As shown, the higher the ionic conductivity the lower the activation energy. This is expected since E_a is calculated from the conductivity. What Figure 5 does show is that the activation energy of the electrolytes does not change over the temperature range. This may indicate the solid gel is homogenous.

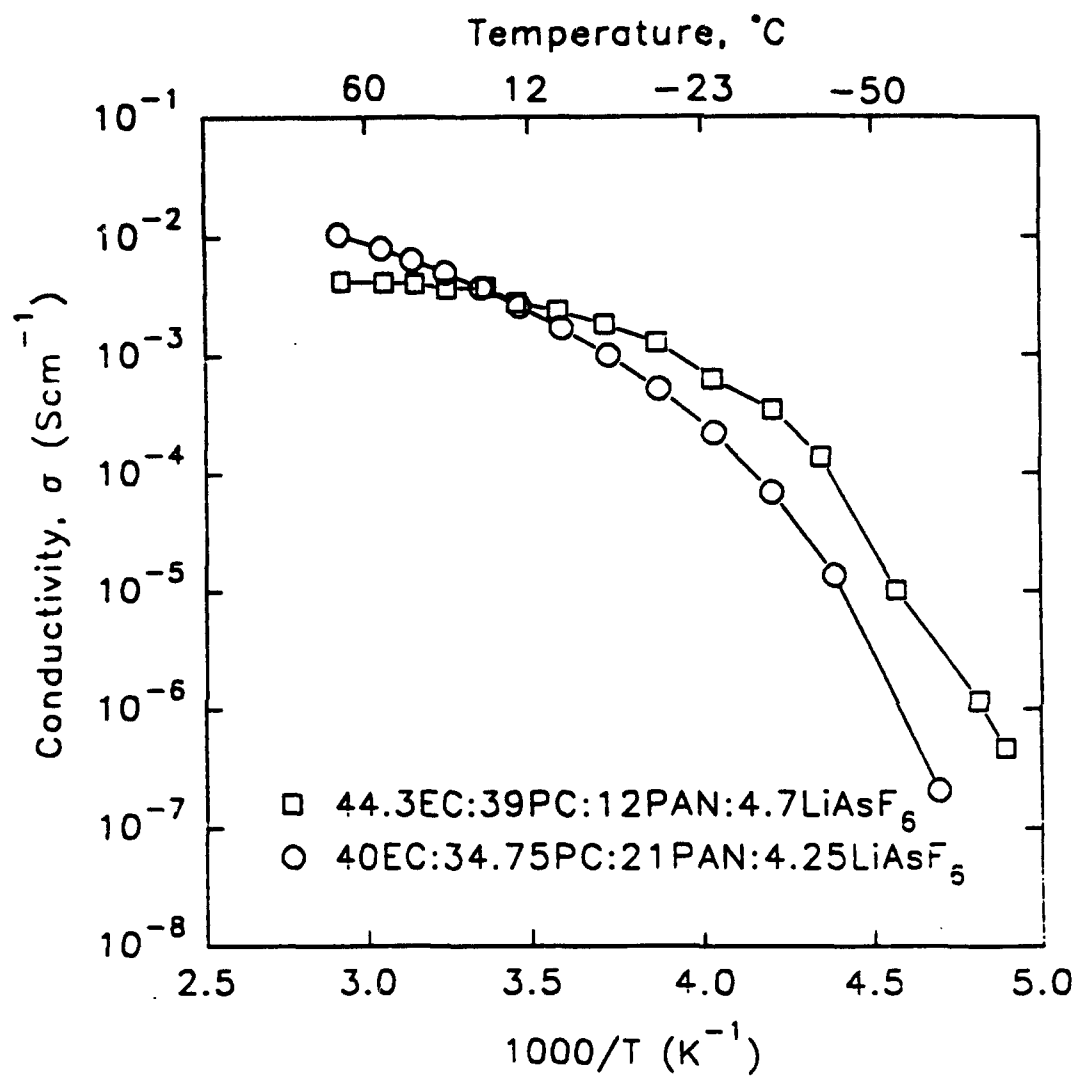


Figure 4. Arrhenius plot of electrolyte conductivities.

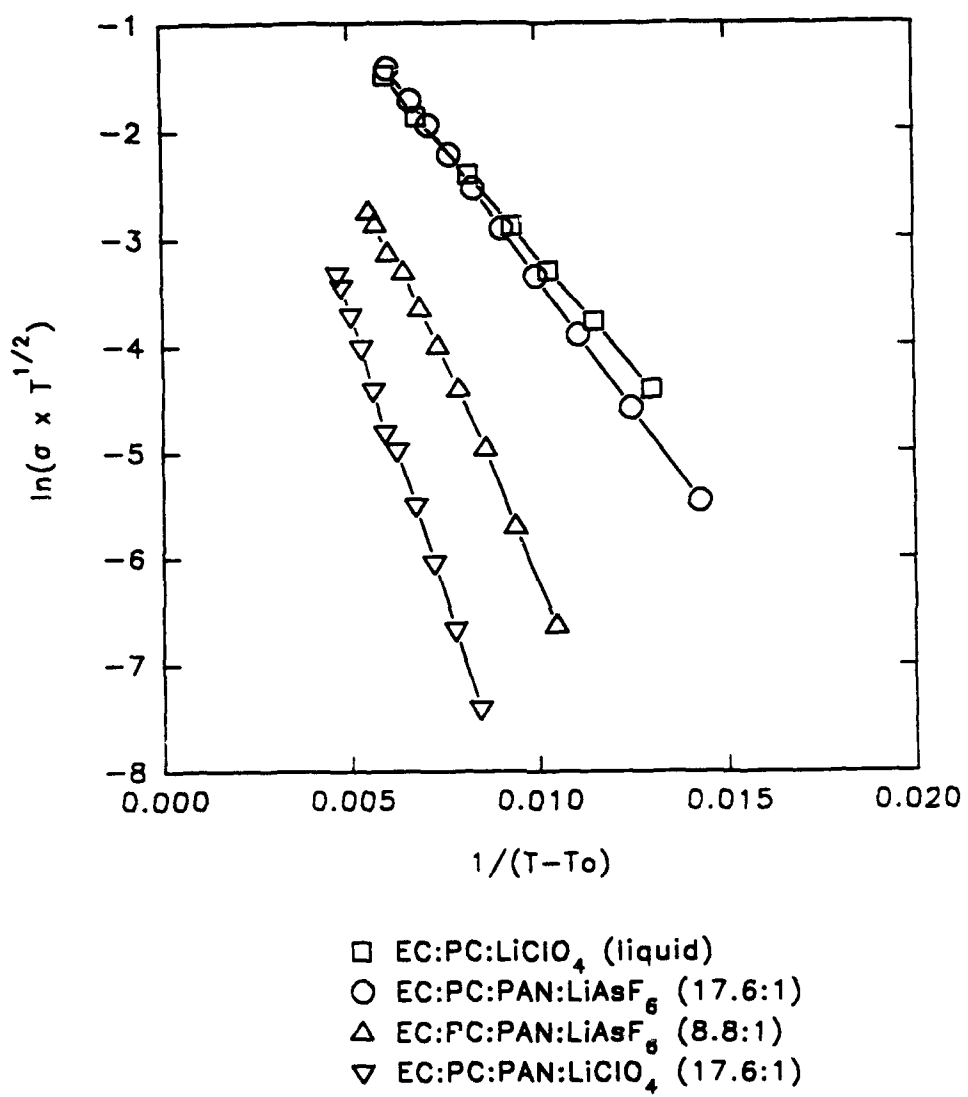


Figure 5. VTF Plot.

CONCLUSIONS

It can be concluded from this study that solid gel polymers based on PAN and LiX salt complexes possess adequate ionic conductivities to be used in lithium rechargeable batteries. The next logical step in the development of these electrolytes is to study their lithium stability and interfacial properties and their use in actual anode/electrolyte/cathode configurations.

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